(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 188 574 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
20.03.2002 Bulletin 2002/12

(51) Int Cl.[7]: **B41M 5/00**, B41M 7/00

(21) Application number: **01810887.8**

(22) Date of filing: **13.09.2001**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **15.09.2000 GB 0022617**

(71) Applicants:
- **ILFORD Imaging Switzerland GmbH**
  1723 Marly 1 (CH)
- **Ilford Imaging UK**
  Knutsford, Cheshire WA16 7JL (GB)

(72) Inventors:
- **King, Jeffrey Ronald**
  Holmes Chapel, Cheshire CW4 7JB (GB)
- **Leggett, Simon Richard John**
  Farnham, Surrey GU9 7BL (GB)

(54) Recording material and recording method

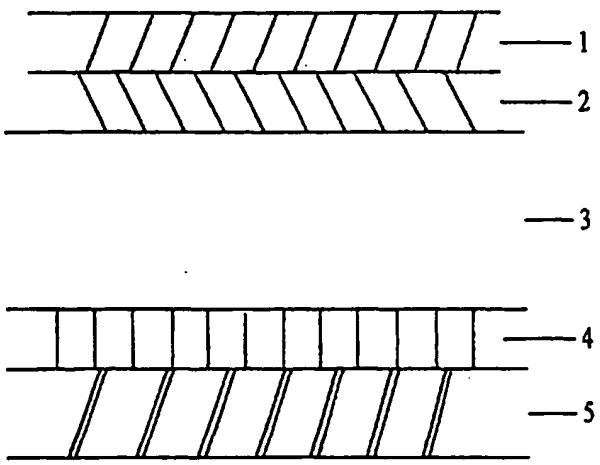
(57) A recording material is provided which comprises in order:

1. A sealing layer comprising a particulate polymer characterised by a film forming temperature of between 60° C and 160° C and an average particle size between 1 µm and 50 µm together with at least one binder,
2. at least one ink receiving layer,
3. a polymeric substrate,
4. an adhesive layer,

and
5. a release liner.

There is also provided a method for treatment of images on the recording material of the invention wherein the printed image is heated after printing to seal the layer comprising the particulate polymer to provide a robust image protecting coating. Preferably the printed image is heated under pressure with the image surface in contact with a second, inert sheet, which is held against the image surface of the material by passing through a laminator.

FIGURE 1



EP 1 188 574 A2

Description

Technical Field

[0001] This invention relates to a recording material and to a method for the treatment of images produced therewith. More particularly, it relates to a recording material and method for use with the ink jet recording system.

Background of the Invention

[0002] The ink jet recording system is a printing and imaging method whereby fine droplets of ink are jetted under computer control and deposited on to a recording material such as a paper sheet to record images or letters. The ink jet recording system has features such as high speed and flexibility and is inexpensive and convenient, particularly in a case where the number of copies is relatively small. There is considerable interest in ink jet printing for various display purposes such as posters, billboards, vehicle graphics, and the like.

[0003] Hitherto ink jet prints for display purposes have been prepared by printing on to a recording material having at least one ink-receiving layer formed on one side of a suitable support and an adhesive layer formed on the other side of the support, and a release sheet integrated thereto to cover the adhesive layer. The purpose of the receiving layer is to take up the ink rapidly and provide good image quality. The purpose of the adhesive layer is to attach the display to a suitable backing such as a support for a display or, in the case of vehicle graphics, to the body of the vehicle. The purpose of the release sheet or liner is to protect the adhesive until it is required for use. One problem with images produced using such materials is that they can be insufficiently robust to handling, and that the image or the receiving layer on which it is printed is sensitive to rubbing, scratching, and staining particularly when wet since the binder for the ink-receptive layer generally comprises water-soluble or water-swellable components.

[0004] Several methods of overcoming this poor robustness are known. For instance various additional coatings and treatments for ink-receiving layers have been proposed, such as lacquers or varnishes which have to be applied after printing the image, thus requiring additional equipment. Another method of improving the robustness of printed images is by lamination, that is to say by covering them with a protective transparent overlay, which is commonly attached to the surface of the image receiving layer with an adhesive activated by heat, pressure, or both. This is particularly common for images intended for external display. The overlay acts as a physical protection for the image and seals it from ingress of water.

[0005] However, lamination is expensive because additional materials are required together with additional handling and equipment, and there is considerable interest in finding a cheaper and simpler method of increasing the robustness of images produced using aqueous inks. We have devised an ink jet recording material and a method, which provides images adequately robust for external display purposes.

Detailed Description of the Invention

[0006] According to the present invention there is provided a recording material which comprises in order:

1) A sealing layer comprising a particulate polymer characterised by a film forming temperature of between 60° C and 160° C, preferably between 60° C and 140° C, and an average particle size between 1 μm and 50 μm together with at least one binder,
2) at least one ink-receiving layer,
3) a polymeric substrate,
4) an adhesive layer,
and
5) a release liner.

[0007] Figure 1 shows a cross section through the material of the invention. In this figure (1) is the sealing layer comprising the particulate polymer, (2) is the ink-receiving layer, which is hereinafter referred to as the ink-receiving layer, (3) is the substrate, (4) is the adhesive layer, and (5) is the release liner.

[0008] Suitable particulate polymers for the sealing layer (1) include any film-forming thermoplastics dispersion, for example a dispersion of polyurethane, low density polyethylene, high density polyethylene, polypropylene, polyvinyl acetate, polyvinyl acetate copolymers, styrene/butadiene copolymers, styrene/butadiene/acrylonitrile terpolymers, styrene/(meth)acrylate copolymers, (meth)acrylic polymers, ethylene/(meth)acrylic acid copolymers, ethylene/vinyl chloride copolymers, and mixtures thereof.

A suitable average particle size for the particulate polymer is between about 1 μm and about 50 μm, with a particle size between about 5 μm and about 20 μm being preferable.

[0009] The particulate polymer should have a melt flow index of at least 5, preferably between about 10 and about 100. A particularly suitable particulate polymer comprises low-density polyethylene microspheres having an average diameter of about 12 μm and a melt flow index of 75. Another particularly suitable particulate polymer comprises microspheres of a 7 % acrylic acid/polyethylene copolymer having an average diameter of about 10 μm and a melt flow index of 9. Another suitable particulate polymer comprises low-density polyethylene particles of random shape and a particle size of about 13 μm and a melt flow index of 70. These polymers have melting points between 105° C and 107° C.

[0010] Suitable binders for the sealing layer (1) include polyvinyl alcohol, copolymers of polyvinyl alcohol, carbohydrates such as tragacanth gum or starch, modified carbohydrates such as hydroxyethyl cellulose or carboxymethyl cellulose, polyacrylates, polyvinyl pyrrolidone, gelatine, casein, and mixtures of such binders. A particularly suitable binder is polyvinyl alcohol, which is hereinafter referred to as PVOH. It is to be understood that commercial samples of PVOH are normally prepared by hydrolysis of polyvinyl acetate, and that this hydrolysis does not always go to completion. Thus, a preferred binder is PVOH having a degree of hydrolysis of at least 85 %, preferably of at least 90 %, and a particularly preferred binder is PVOH having a degree of hydrolysis of between about 98 % and about 99 %.

[0011] The coating weight of the sealing layer and the weight ratio between the polymeric particles and the binder may be determined by the desired image quality, gloss, and robustness of the final print. A suitable coating weight for the sealing layer is from about 15 g/m^2 to about 40 g/m^2. A preferred coating weight is between about 15 g/m^2 and about 25 g/m^2. The ratio of the coating weight of the particulate polymer to that of the hydrophilic binder may be from about 20 : 1 to about 1 : 1, but preferably is between about 10 : 1 and about 5 : 1.

[0012] The ink-receiving layer (2) to be formed on the support may comprise any of the known ink-receiving layers known in the art. Preferably, the ink-receiving layer (2) is formed by a composition comprising at least one white pigment or filler and a suitable polymeric binder as the main components. Suitable white pigments and fillers include conventional white inorganic pigments and starch particles. Examples of white inorganic pigments are light calcium carbonate, heavy calcium carbonate, kaolin, talc, calcium sulphate, barium sulphate, titanium dioxide, zinc oxide, zinc sulphide, zinc carbonate, satin white, aluminium silicate, diatomaceous earth, calcium silicate, magnesium silicate, synthetic non-crystalline silica, colloidal silica, colloidal alumina, pseudo-boehmite, aluminium hydroxide, alumina, lithopone, zeolite, hydrolysed halloysite, magnesium carbonate, magnesium hydroxide, clays and the like. Among the above pigments, a porous inorganic pigment is preferred, such as porous non-crystalline synthetic silica, porous magnesium carbonate, or porous alumina.

Porous synthetic non-crystalline silica having a large pore volume is particularly preferred.

The polymeric binder to be used for the ink-receiving layer (2) of the present invention may, for example, be starch or a starch derivative such as oxidized starch, etherified starch or phosphated starch; a cellulose derivative such as carboxymethyl cellulose or hydroxyethyl cellulose; casein, gelatine, tragacanth gum, soybean protein, a polyacrylate, polyvinyl alcohol, a copolymer of polyvinyl alcohol, polyvinyl pyrrolidone, and mixtures of such binders.

Hydrophilic acrylate binders are preferred.

Optionally the ink-receiving layer may also contain a basic or cationic polymer. The cationic or basic polymer may comprise a polymer incorporating primary, secondary, or tertiary amino groups or typical cationic groups such as quaternary ammonium salts. The polymer may, for example, be a polyalkylene polyamide, a ring-opened polymer of ethyleneimine, a homopolymer of a cationic vinyl polymer or a copolymer thereof with another polymerizable monomer, a homopolymer of a basic nitrogen containing acrylate or other vinyl monomer or a copolymer thereof with another polymerizable monomer.

A preferred polymer is a copolymer of vinyl imidazole with vinyl pyrrolidone.

The coating weight of the ink-receiving layer may be determined by the quantity of ink to be printed. A suitable coating weight for the ink-receiving layer is from about 5 g/m^2 to about 50 g/m^2. A preferred coating weight for the ink-receiving layer is from about 15 g/m^2 to about 40 g/m^2.

[0013] Further, it is possible to provide two or more ink-receiving layers on the support.

[0014] The heat sealing layer and receiving layer or layers of the invention may advantageously also comprise additives which are commonly added to ink-receiving layers such as surfactants to improve coating quality, cross linking agents, optical brightening agents, tinting agents, and biocides or preservatives. Suitable cross-linking agents for the preferred polyvinyl alcohol binders of the invention include boric acid and aldehydes such as glyoxal or glutaraldehyde.

[0015] Suitable polymeric substrates (3) for the materials of the invention include any of those commonly used for printing and imaging media, especially cellulose acetates, polyethylene, polypropylene, polyvinyl chloride, and polyesters including polyethylene terephthalate, polybutylene terephthalate, and polyethylene naphthalate. Opaque substrates such as voided polyester and poly vinyl chloride are particularly useful. A preferred substrate is polyvinyl chloride. The substrate may contain other additives as are known in the art. It is especially preferred to use plasticisers such as phthalate esters, phosphate esters, or polymeric plasticisers and stabilisers such as tin stabilisers and lead stabilisers with the preferred polyvinyl chloride substrates of the invention.

[0016] Suitable adhesives (4) include solvent type and aqueous type adhesives. Aqueous adhesives of the emulsion

type obtained by emulsion polymerisation in water employing a surface-active agent are well known. Preferably, the adhesive (4) is a pressure sensitive organic solvent type adhesive such as a rubber type adhesive or an acrylic resin type adhesive. The main material of the rubber-type adhesive is natural rubber or styrene-butadiene rubber. To the natural rubber, a resin or a plasticiser may be incorporated, and a suitable solvent for coating such as n-hexane. The acrylic resin type adhesive may be prepared by polymerising an acrylic monomer such as 2-ethylhexyl acrylate, butyl acrylate, ethyl acrylate, or β-hydroxyethyl acrylate, in an organic solvent. Further, in order to improve the physical properties such as the heat resistance and the solvent resistance of the adhesive, a cross linking agent of isocyanate type, melamine type or metal chelate type may be reacted to the above material for the cross linking reaction, or a pigment such as silica, kaolin, clay, calcium carbonate, aluminium hydroxide, zinc oxide, titanium dioxide, melamine resin particles or starch particles, may be incorporated to the above material. Depending upon the particular purpose for which the ink jet recording sheet is employed other additives may be incorporated in the adhesive layer (4) including a water soluble polymer, a petroleum type resin, a paraffin wax, a fatty acid or its derivative, a higher alcohol, a metal soap, or a silicone as well as an antistatic agent, a thickener, a dispersant, a preservative, an antioxidant or a defoaming agent.

[0017] Suitable materials for the release sheet (5) include wood free paper, kraft paper, glassine paper, impregnated paper, or a plastic film such as a polyester film or a polyamide film. These may be coated with a silicone resin or polytetrafluoroethylene as a release agent. In the case of a paper type base material, a thermoplastic resin may preferably be laminated on the base material to form a smooth surface so as to improve the peeling properties. Preferably, the release sheet is a siliconised plain kraft paper weighing about 100 g/m^2. The release sheet is releasably adhered to the rest of the material, and is selected on such a basis that the release sheet has an adhesive force sufficiently strong not to be peeled during transportation in an ink jet recording apparatus or during sealing of the heat sealing layer but weak enough to peel easily when it is desired to attach the printed image to its display panel.

[0018] Although other methods for the preparation of the materials of the present invention are possible, it is preferable to employ a method wherein the image-receiving layer or layers (2) together with the sealing layer (1) are coated either simultaneously or separately on to a material comprising the substrate (3), the adhesive layer (4), and the release sheet (5). Alternatively the sealing layer (1) may be coated on to a existing ink jet medium which comprises the release liner (5), adhesive layer (4), substrate (3), and image-receiving layer or layers (2). Any convenient coating method may be used for the preparation of the materials of the present invention, such as blade coating, knife coating, slide coating and curtain coating.

[0019] It may be advantageous to treat the surface of the substrate (3) to assist adhesion of the image-receiving layer (2). This treatment may take the form of a surface modification technique such as flame or corona treatment, buffing, or the like, but preferably may involve the application of a chemical priming or subbing layer. Such adhesion promoting treatments are well known.

[0020] Any convenient ink jet printer may be used for printing on the materials of the invention, for example a continuous printer or a piezoelectric or thermal drop-on-demand printer. Suitable jetting inks include aqueous inks and those based on organic solvents such as 2-butanone, ester solvents, and mineral oils. Suitable colorants for these inks include dyes or pigments. Preferred inks for the invention are pigmented aqueous inks.

The recording materials of the invention may also be used with other printing methods as are known in the art, or as writing or drawing materials for use with felt tip pens and the like.

The materials of the invention are particularly suitable for use in a printing process wherein the printed image is heated after printing to seal the sealing layer to provide a robust image protecting coating.

[0021] Therefore, according to this aspect of this invention, the printed image is heated after printing to seal the sealing layer. The heating process may use any convenient method, such as heated air, contact with a heated surface, or infrared or microwave radiation. Alternatively, the print may be heated under pressure in contact with a heated surface or by passing it between heated rollers. A suitable temperature is between about 80° C and about 180° C, preferably between about 80° C and about 160° C, particularly preferably between about 100° C and about 120° C. It is important that this heating process does not affect the components of the substrate, adhesive layer, and release liner. One of the advantages of the preferred particulate polymers of the heat-sealing layer of the invention is that the softening points are relatively low and thus the temperature and time needed to seal them are minimised.

[0022] According to another aspect of the invention, the printed image is heated under pressure with the image surface in contact with a second, inert sheet, which is held against the image protective layer of the material. The inert sheet does not adhere to the material, but protects it from the means used to apply the pressure. Suitable inert sheets include polyester films, polyamide films, and casting papers. The inert sheet may be treated with silicones or polytetrafluoroethylene to enhance the release properties. Furthermore, a suitable choice of the inert sheet may be used to produce a desired appearance to the final image such as the use of a smooth inert sheet, which will impart a high gloss to the image, or a textured sheet, which will produce a textured finish.

Preferably, according to this aspect of this invention, the printed image is heated by passing through a laminator. By laminator is meant a device, which is normally used for the lamination of printed images, which comprises a means of

heating and pressing together the image and the cover sheet, commonly by passing them through a nip between a pair of heated rollers.

[0023] It is believed that the dye or pigment components of the ink are substantially retained within the sealing layer after printing, thus separating them from the liquid ink vehicle, which is largely transferred to the ink-receiving layer. The colorant components then become encapsulated within the sealing layer after heating.

[0024] The materials and method of this invention are suitable for many uses where robustness of an ink jet image is important, such as posters, displays, vehicle graphics, and the like.

[0025] The following Examples will serve to illustrate the invention.

Examples

Example 1

[0026] A material according to the invention was prepared as follows:
A support comprising a monomerically plasticised polyvinyl chloride substrate, an acrylic, water based pressure sensitive adhesive layer, and a 100 g/m^2 siliconised plain kraft paper release sheet was coated with the following layers in order:

a) An adhesion-promoting layer formulated using the following components: A formulation for an adhesion-promoting layer was prepared using the components of Table 1:

Table 1

Component	Quantity
Acrylic modified polyurethane dispersion	900 g
Aziridine cross linker	8 g
Siloxane surfactant	2 g
Water	90 g

The polyurethane dispersion was obtained from Zeneca under the trade name Neorez R973 and the cross linker from Zeneca under the trade name CX100.
The surfactant was a commercial sample from Byk Chemie under the trade name Byk 348.
The total solid concentration of the formulation was 37 %. It was coated to give a coating weight of 2 g/m^2.

b) An ink-receiving layer was formulated using the components of Table 2:

Table 2

Component	Quantity
Synthetic silica	95.3 g
Siloxane surfactant as for adhesion layer	1.5 g
Acrylic solution polymer	212.6 g
PVI/PVP polymer	212.6 g
Water	478.0 g

The synthetic silica had a particle size of 12 µm and it is available under the trade name of Sylojet P412 from Grace Davidson. The acrylic polymer was from Worle under the trade name of Worlecryl 8040. The PVI/PVP polymer is a vinyl imidazole/vinyl pyrrolidone copolymer from BASF under the trade name Luvitec VP155K72W. The total solid concentration of the formulation was 22.42 %. It was coated to give a coating weight of approximately 30 g/m^2.

c) A heat-sealing layer was formulated using the components of Table 3:

Table 3

Component	Quantity
99 %PVOH (10 % solution)	400 g
Siloxane surfactant as for adhesion layer	2 g
Acrylic modified polyethylene beads	250 g
Water	478 g

The polyvinyl alcohol was obtained from Harco under the trade name of Mowiol 28-99. The acrylic modified polyethylene beads were obtained from Sumitomo under the trade name EA209 flowbeads.
The total solid concentration of the formulation was 29.2 %. It was coated to give a coating weight of approximately 29 g/m^2.

[0027] A test pattern was printed on the material using ILFORD Archiva Extreme pigmented aqueous inks, available from ILFORD Imaging UK, on a Novajet III printer. The image was sealed by passing it through a Seal 600 laminator with the image face in contact with a 125 µm thickness smooth polyester film available under the trade name Melinex O. A bright, glossy image was produced, resistant to water and rubbing.

Example 2

[0028] A sample of the material produced in example 1 was printed with ILFORD Archiva dyed aqueous inks, available from ILFORD Imaging Switzerland GmbH, using an Epson Pro E printer and sealed as in example 1. A bright glossy image was produced, resistant to water and rubbing.

Example 3

[0029] A sample of the material produced in example 1 was printed using aqueous inks on an Epson 3000 desktop printer. The image was sealed using a GBC 1200 desktop laminator at a set temperature of 120° C with the image face in contact with a smooth polyester film as in example 1. A bright glossy image was produced, resistant to water and rubbing.

Example 4

[0030] A sample of the material produced in example 1 was printed with mineral oil based inks according to patent application WO 96-24'642 and sealed as in example 3. A bright glossy image was produced, resistant to water and rubbing.

Example 5

[0031] A material according to the invention was prepared as follows:
A support comprising a polymerically plasticised cast polyvinyl chloride substrate, an acrylic, water based pressure sensitive adhesive layer, and a 100 g/m^2 siliconised plain kraft paper release sheet was coated with the following layers in order:

a) The formulation for the adhesion-promoting layer was the same as in example 1.

b) An ink-receiving layer was formulated using the components of Table 4:

Table 4

Component	Quantity
Synthetic silica	111.5g
Siloxane surfactant as for adhesion layer	2.2 g
Acrylic solution polymer	310.3 g

Table 4 (continued)

Component	Quantity
PVI/PVP polymer	185.7 g
Water	390.3 g

The synthetic silica had a particle size of 12 μm and it is available under the trade name of Sylojet P412 from Grace Davidson. The acrylic polymer was from Worle under the trade name of Worlecryl 8025. The PVI/PVP polymer is a vinyl imidazole/vinyl pyrrolidone copolymer from BASF under the trade name Luvitec VP155K72W. The total solid concentration of the formulation was 22.5 %.

c) A heat-sealing layer was formulated using the components of Table 5:

Table 5

Component	Quantity
99 %PVOH (30 % solution)	124.3 g
Siloxane surfactant as for adhesion layer	2.0 g
Polyethylene beads	310.8 g
Water	562.9 g

The polyvinyl alcohol was obtained from Harco under the trade name of Mowiol 4-88. The polyethylene beads with a mean particle size of 6 μm were obtained from DuPont under the trade name Coathylene.
The total solid concentration of the formulation was 35 %.

[0032] The three layers were coated simultaneously onto the substrate using a slide bead coating technique.
[0033] The coating weights (as solids) of the three layers were:

a) 4 g/m^2
b) 12 g/m^2
c) 18 g/m^2

[0034] A test pattern was printed and the image was sealed as in example 1. A bright, glossy image was produced, resistant to water and rubbing, and which could be adhered to an uneven surface without compromising the quality of the image.

Claims

1. A recording material, which comprises in order:

   1) a sealing layer comprising a particulate polymer **characterised by** a film forming temperature of between 60° C and 160° C and an average particle size between 1 μm and 50 μm together with at least one binder,
   2) at least one ink-receiving layer,
   3) a polymeric substrate,
   4) an adhesive layer
   and
   5) a release liner.

2. A recording material according to claim 1 wherein the particulate polymer has an average particle size between 5 μm and 20 μm.

3. A recording material according to either of claims 1 or 2 wherein the particulate polymeric dispersion comprises low density polyethylene.

4. A recording material according to any of claims 1 to 3 wherein the binder for the sealing layer is at least one of

polyvinyl alcohol, a copolymer of polyvinyl alcohol, tragacanth gum, casein, starch, hydroxyethyl cellulose, carboxymethyl cellulose, a polyacrylate, polyvinyl pyrrolidone and gelatine.

5. A recording material according to any of claims 1 to 4 wherein the ink-receiving layer is formed by a composition comprising at least one white pigment and a polymeric binder.

6. A recording material according to claim 5 wherein the white pigment is at least one of calcium carbonate, kaolin, talc, calcium sulphate, barium sulphate, titanium dioxide, zinc oxide, zinc sulphide, zinc carbonate, satin white, aluminium silicate, diatomaceous earth, calcium silicate, magnesium silicate, synthetic non-crystalline silica, colloidal silica, colloidal alumina, pseudo-boehmite, aluminium hydroxide, alumina, lithopone, zeolite, hydrolysed halloysite, magnesium carbonate and magnesium hydroxide.

7. A recording material according to any of claims 1 to 6 wherein the polymeric substrate is cellulose acetate, polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate, polybutylene terephthalate and polyethylene naphthalate.

8. A recording material according to claim 6 wherein the polymeric substrate is opaque.

9. A recording material according to claim 8 wherein the opaque polymeric substrate is plasticised polyvinyl chloride.

10. A recording material according to any of claims 1 to 9 wherein the release liner comprises kraft paper, glassine paper, impregnated paper, polyester film or polyamide film.

11. A printing method whereby an image printed on a recording material according to any of claims 1 to 10 is heated after printing to seal the porous sealing layer to provide a robust protective surface.

12. A printing method according to claim 11 whereby the material is heated to between 80° C and 180° C.

13. A printing method according to claim 11 or 12 whereby the material is printed using the ink jet printing process.

14. A printing method according to any of claims 11 to 13 whereby the printed material is heated under pressure with the image surface in contact with a second, inert sheet, which is held against the image protective layer of the material.

15. A printing method according to claim 14 whereby the printed material and inert sheet are heated under pressure by passing them through a laminator.

FIGURE 1